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Effect of Sn Incorporation in ZnS thin Film Synthesized by CBD

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Abstract. Polycrystalline zinc sulphide (ZnS) and tin (Sn) doped ZnS thin film was synthesized on glass substrate by chemical bath deposition technique. SEM micrograph shows formation of polycrystalline grains on the surface. The incorporation of Sn was confirmed form EDX measurement. The measured bandgap energy was ~3.70 eV for pure ZnS was shifted on higher side due to Sn incorporation.

1. Introduction

Recent investigations have evoked considerable interest in ZnS thin films due to their vast potential for use in thin film devices such as photoluminescent and electroluminescent devices and more recently as *n*-type window layer heterojunction solar cells. ZnS with wurtzite structure is a direct wide band gap (3.7 eV) semiconductor [1-4], that is one of the most important materials in photonics owing to its high transmittance in visible range and its high index of refraction (about 2.2). ZnS is also an important phosphor host lattice material used in electroluminescent devices (ELD). This is because of its large band gap that is enough to emit visible light without absorption and the efficient transport of high energy electrons. It is the materials of reference to test several theoretical models in condensed matter physics [5-6]. The present investigation is based on the synthesis of ZnS thin film and their morphological and optical properties. The effect of Sn^{2+} doping on optical properties of ZnS is also presented. The injection of Sn, that substitutes Zn cations, usually leads to the creation of additional polarizability at the film–glass frontier.

2. Experimental

Sn doped *ZnS* thin film was deposited on precleaned glass substrate using CBD. The substrate was etched in HF solution for 30 minutes and then cleaned ultrasonically in acetone and deionized water. Finally it was dried at 90^{o}C for one hour. The bath solution used for film deposition was prepared by adding requisite quantity of zinc acetate [$Zn(CH_3COO)_2$] in deionized water. The solution strength was 0.1M. Tin doping was

achieved by adding tin chloride ($SnCl_2,2H_2O$) in the zinc acetate solution. 5% Sn doping was made in the present work. 5 ml triethanolamine (TEA), 30ml ammonia (NH_3) solution, 10 ml of 0.33 M tri-sodium citrate ($C_6H_5Na_3O_7$) and 50 ml of 0.1 M thiourea [$CS(NH_2)_2$] were added to the reaction medium. The mixture was stirred properly to make homogeneous solution having pH~11.

The substrate was dipped in the solution for 72 hours. A thin coating with white coloration appeared on the substrate. For tin doped films, the color was slightly off-white. The coated substrate was removed at the end of deposition, washed in deionized water, dried in air room temperature. Finally they were subjected to morphological and optical characterization.

The film thickness was measured using fiber optic spectrophotometer (Ocean Optics International). Light beam form tungsten source at normal incidence was used to measure the reflectance. Scanning electron microscopy (SEM) was used to illustrate the formation of crystallites on the film surface. EDX measurement was done to study the composition of the film. The optical absorbance at normal incidence was measured in a UV-VIS spectrophotometer (Shimadzu, UV-1800) at room temperature. The spectra were recorded by using similar glass as a reference and hence the absorption due to the film only was obtained.

3. Results and Discussions

3.1 Film thickness

Figure 1 shows the spectrum obtained from fiber optic spectrophotometer. Figure shows the dependence of reflectance $(R\%)$ against wavelength (λ). The film thickness (t) was calculated using the relation

$$t = \frac{m}{2D\mu}$$

where m is the number of fringe, μ is the refractive index of the material and $D = \lambda_1^{-1} - \lambda_2^{-1}$. λ_1 and λ_2 are the wavelengths of the n th and $(n+m)$ th fringe. The maximum values corresponds to bright fringes and minimum values corresponds to dark fringes. The figure shows three fringes (the maximus are marked). The film thickness evaluated was ~ 1.53 μm. The refractive index value of 2.2 was used for finding the thickness.

3.2. Morphology and EDX

Figure 2 shows the SEM micrograph of ZnS while Figure 3 shows the SEM image for Sn:ZnS. Prior to imaging, the films were sputtered with thin gold film to avoid charging. The formation of sub-micrometer crystallites distributed more or less uniformly over the surface is evident from the figure. Some holes indicating porosity and agglomeration of small crystallites also seem to be present in certain regions on the film surface.

Figure 4 shows the energy dispersive X-ray (EDX) spectrum of Sn:ZnS film while Figure 5 shows the same for Sn:ZnS. The spectrum reveals the incorporation of Sn in the doped film. The silicon and oxygen signal appears from the substrate. Contamination of carbon and sulphur impurity element was detected in the films. Oxygen incorporation was form the substrate used.

3.3. Optical band gap

The optical absorbance spectrum was measured in the wavelength range of 500–800 nm using a Shimadzu spectrophotometer (Model -1800). Theory of optical absorption gives the relationship between the absorption coefficients α and the photon energy $h\nu$ for direct allowed transition as

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

where A is a function of index of refraction and hole/electron effective masses**.** The direct band gap is determined using this equation when linear portion of the $(\alpha h\nu)^2$ against $h\nu$ plot is extrapolated to intersect the energy axis at α =0. Plot of $(\alpha h\nu)^2$ against $h\nu$ for ZnS film is shown in Figure 6. The value of optical band gap evaluated was ~3.70 eV. For tin doping the optical band gap was ~3.94eV. The enhancement of band gap might be due quantum confinement arising from lowering of particle size.

4. Conclusions

Sn doped ZnS thin film could be successfully synthesized by CBD technique. The films are polycrystalline as revealed from SEM study. The bandgap energy value of ~3.70 eV for pure ZnS film was shifted to higher energy side due to tin doping indicating quantum confinement arising from tin incorporation. The incorporation of Sn was confirmed from EDX measurement.

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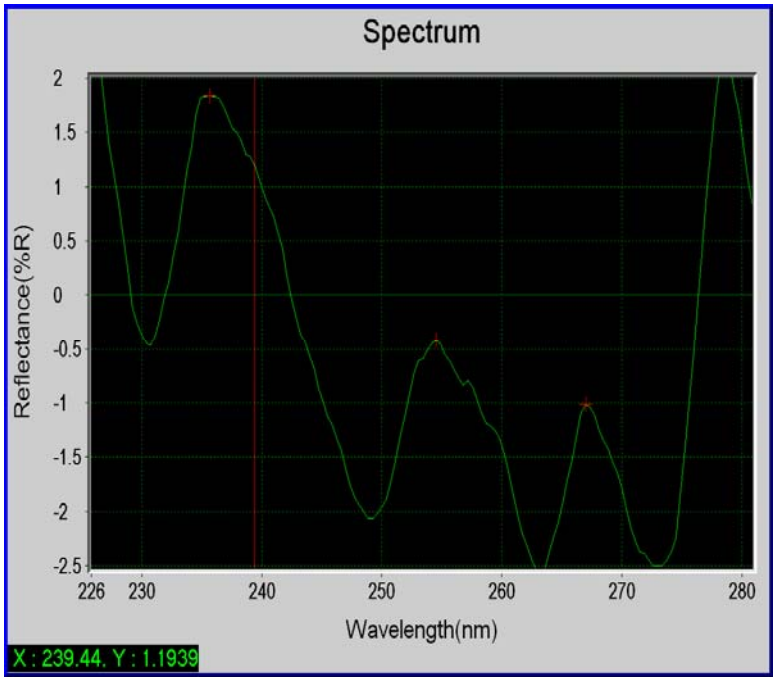

Figure 1. Reflectance pattern of Sn:ZnS thin film

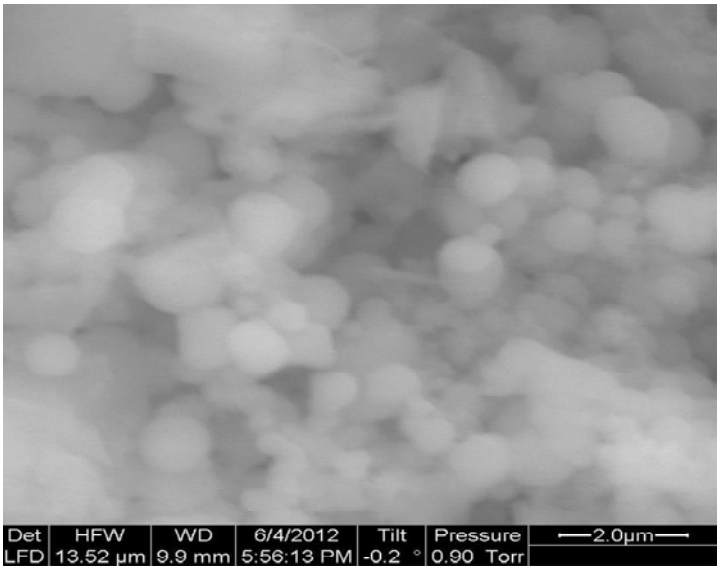

Figure 2. SEM of ZnS film

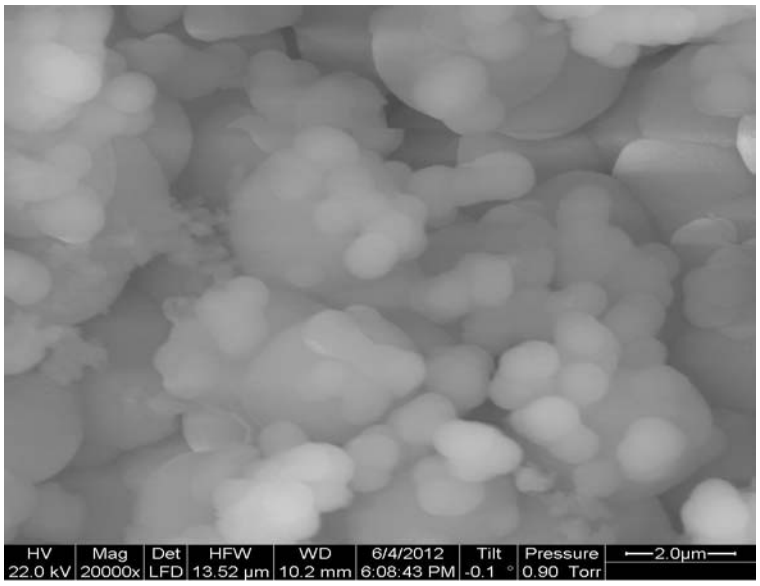

Figure 3. SEM of Sn:ZnS film

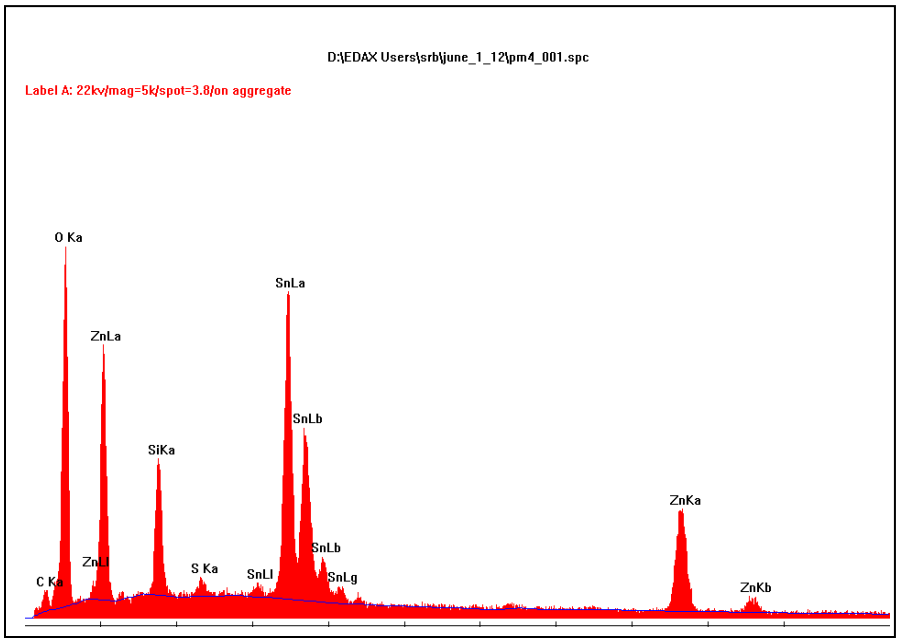

Figure 4. EDX spectrum of Sn:ZnS

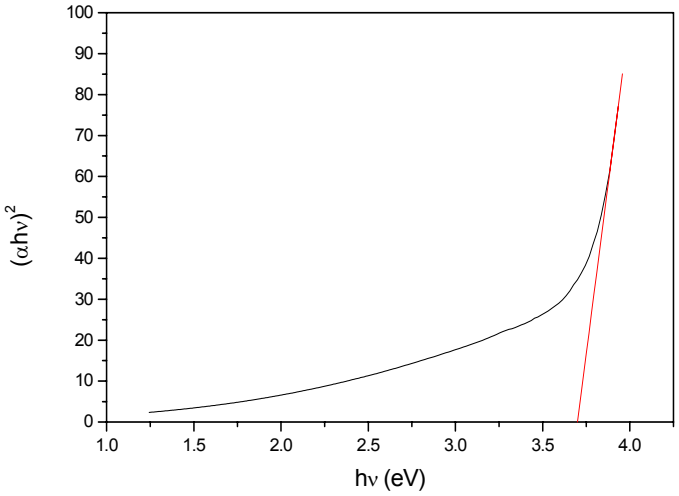

Figure 5. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for ZnS

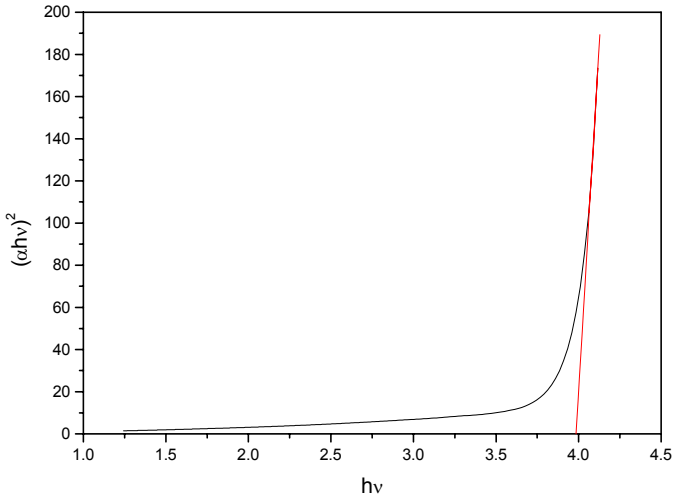

Figure 6. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for Sn:ZnS